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(54) Title: HYDROCARBON CONVERSION PROCESS

(57) Abstract: The invention provides a hydrocarbon conversion process for converting olefins to longer chain hydrocarbons, the process using a catalyst system including a non-nickel transition metal derived catalyst and one or more ionic liquids at a reaction temperature of between 10°C and 130°C and a reaction pressure of up to 100 Bar. The hydrocarbon conversion process may be oligomerisation and trimerisation.

## HYDROCARBON CONVERSION PROCESS

### Background Of The Invention

5        This invention relates to a hydrocarbon conversion process. More particularly, this invention relates to a hydrocarbon conversion process for the oligomerisation of olefins and derivatives thereof.

10        The oligomerisation of olefins, primarily  $\alpha$ -olefins, with chromium catalysts has been extensively studied. More specifically, a number of chromium catalysts have been developed and used to trimerise olefins. In this regard, the trimerisation of ethylene to 1-hexene is significant since, in addition to its use as a specific chemical, 1-hexene is extensively used in polymerisation processes either as a monomer or co monomer. Furthermore, the trimeric products derived from longer  
15 chain olefins could be well utilized as synthetic lubricants (e.g. polyalphaolefins / PAO's), as well as various other applications such as drilling muds, and as feedstock to prepare detergents and plasticizers.

20        Known chromium-based processes for the trimerisation of ethylene to 1-hexene include:

25        a)    A process disclosed in US Patent No. 4,668,838, in which olefins are trimerised by passing the olefin in contact with a catalyst comprising the reaction product of a chromium compound, an organoaluminium compound hydrolysed with a specific amount of water and a donor ligand selected from hydrocarbyl isonitriles, amines and ethers;

30        b)    European Patent No. 0 416 304 discloses the trimerisation of olefins by chromium-containing compounds, such as, for example, chromium pyrrolides that are prepared by forming a mixture of a chromium salt, a metal amide and an electron pair donor solvent, such as, for example, an ether. These chromium catalysts can be used either unsupported or supported on an inorganic oxide;

c) European Patent No. 0 668 105 discloses a process to trimerise ethylene to 1-hexene comprising contacting ethylene with a stabilized catalyst system comprising a chromium source, a pyrrole-containing compound, a metal alkyl and an aromatic compound;

5

d) European Patent No. 0 706 983 discloses a process for preparing an  $\alpha$ -olefin oligomer which comprises oligomerising an  $\alpha$ -olefin in a saturated hydrocarbon solvent in the presence of a chromium-based catalyst system comprising a combination of at least a chromium compound, an amine or metal amide, an alkylaluminium compound and a non-coordinating Lewis acid-containing compound based on an element selected from groups IIIB, IVB, VB and VIB of the periodic table;

10

e) European Patent No. 0 699 648 discloses a process for producing 1-hexene which comprises trimerising ethylene in a 1-hexene solvent in the presence of a catalyst system obtainable by contacting in a 1-hexene solvent a chromium-containing compound, trialkylaluminium or dialkylaluminium hydride, a pyrrole compound or derivative thereof and a group 13 (III B) or group 14 (IV B) halogen compound; and

15

20

f) US Patent No. 5,811,618 discloses a process for the trimerisation of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminoxane and a polydentate phosphine, arsenic and/or stibine coordination complex of a chromium salt, such that 1-hexene is formed.

25

Also, WO 98/47616 discloses that ionic liquids may be used as solvent and/or activator during the oligomerisation of olefins with a nickel complex as catalyst.

Heterogeneous catalysts systems are often selected over homogeneous catalyst systems due to relative ease of recovering and recycling such catalyst systems. However, the process of trimerisation of ethylene using chromium catalysts supported on an inorganic oxide has problems of insufficient activity, poor selectivity  
5 towards the intended trimeric product and leads to unsatisfactory levels of polyethylene by-product.

Trimerisation processes using unsupported chromium catalyst systems  
10 involve the use of unsaturated hydrocarbon and/or saturated hydrocarbon and/or aromatic solvents. Consequently, recovery of chromium compounds from the reactor effluent stream requires several sequential steps.

A need has thus been identified for a catalyst system capable of being easily  
15 recovered and recycled, without compromising the advantages associated with homogeneous systems.

Non-aqueous room-temperature ionic liquids are generally composed of large organic cations associated with inorganic or organic anions. They can be described  
20 as mixtures of salts that are liquid at temperatures below the individual melting points of the components.

Ionic liquids are either organic salts or mixtures consisting of at least one organic component, the most common organic salts used being alkylammonium,  
25 alkylphosphonium, N-alkylpyridinium, and N,N -dialkylimidazolium as cations, associated with inorganic or organic anions.

The two basic methods for the preparation of ionic liquids are metathesis of a halide salt with, for instance, a silver, group 1 metal or ammonium salt of the desired  
30 anion, and secondly acid-base neutralization reactions.

## DETAILED DESCRIPTION OF THE INVENTION

Thus, according to first aspect of the invention, there is provided a  
5 hydrocarbon conversion process using a catalyst system including a non-nickel  
transition metal derived catalyst and one or more ionic liquids.

According to a second aspect of the invention, there is provided an  
oligomerisation process using a catalyst system including a non-nickel transition  
10 metal derived catalyst and one or more ionic liquids.

The ionic liquids may be liquid at room temperature, i.e. at below 50°C,  
typically at below 30°C. Usually the ionic liquids are liquid at between 15°C and  
25°C.

15 The ionic liquids may be non-aqueous ionic liquids.

The ionic liquids may be used as a solvent / co-solvent or activator for the  
catalyst system of the invention.

20 It is believed that the physical properties of the ionic liquids which make them  
suitable for an oligomerisation catalyst system include them being:

- (1) good solvents for a wide range of both inorganic and organic  
materials;
- 25 (2) composed of poorly coordinating ions, thereby having the  
potential to be highly polar yet non-coordinating solvents;
- (3) immiscible with a number of organic solvents and providing a  
non-aqueous, polar alternative for two-phase systems; and
- (4) non-volatile, hence being useable in high-vacuum systems.

It is further believed that the anions are essentially responsible for the chemical properties of ionic liquids, the most important of which, for coordination chemists, is the coordinating ability and/or reactivity of anions toward the metal centre of a complex. These properties are believed to depend on the nature of the anions themselves, such as the size and charge and also on the hardness of the metal centre, its oxidation state, and its surrounding ligands.

The ionic liquids of the process of the invention may include as cation an organic halide salt such as a quaternary ammonium salt, an imidazoline or alkyl-substituted imidazoline salt, a pyridinium or alkyl-substituted pyridinium salt, a sulfonium or alkylsulfonium salt, or a phosphonium or alkyl-substituted phosphonium salt, or other suitable anion leading to ionic liquids having the desired properties.

The ionic liquids of the process of the invention may include as anion compounds of the formula  $R_nMX_{3-n}$ , or  $R_mM_2X_{6-m}$  wherein

R is a  $C_1 - C_6$  alkyl (or iso-alkyl) radical;

M is aluminium, gallium, boron or iron (III);

X is a halogen atom;

n is 0, 1, 2 or 3; and

m is 1, 2 or 3.

The metal component of the anion compounds, M, is typically aluminium and m and/or n is typically three; therefore, the anion is typically an alkylaluminium compound. One such alkylaluminium useful as an anion for the process of the invention is triethylaluminium.

In some embodiments of the process of the invention, the anion is an alkylaluminoxane such as methylaluminoxane, or a borate anion such as  $B(C_6F_5)_4^-$ .

Miscibilities of the corresponding ionic liquids with organic reactants may be altered by varying the alkyl chain length of the cation, when appropriate.

The ionic liquids of the process of the invention may include as anion an alkylaluminoxane or iso-alkylaluminoxane. The alkylaluminoxane may be methylaluminoxane, also known as MAO.

5 The ionic liquids of the process of the invention may include as anion tin and germanium halides,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{FSO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{CF}_3\text{CO}_2^-$ , copper, ammonium or phosphonium chlorides.

10 The ionic liquids of the process of the invention may include as anion large, weakly coordinating anions such as tetraphenylborate ( $\text{BPh}_4^-$ ) and related anions such as fluorinated derivatives of  $\text{BPh}_4^-$ .

The ionic liquids of the process of the invention may include  $\text{B}(\text{p-C}_6\text{H}_4\text{F})_4^-$ ,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4^-$ , and  $\text{PH}_3\text{BCNBPh}_3^-$ .

15 Other useful anions include 1-carba-*closo*-dodecacarborate ( $\text{CB}_{11}\text{H}_{12}^-$ ) and related anions,  $12\text{-CB}_{11}\text{H}_{11}\text{Cl}^-$ ,  $12\text{-CB}_{11}\text{H}_{11}\text{Br}^-$ ,  $12\text{-CB}_{11}\text{H}_{11}\text{I}^-$ ,  $12\text{-CB}_{11}\text{H}_{11}(\text{C}_6\text{F}_5)^-$ ,  $7,12\text{-CB}_{11}\text{H}_{10}$ ,  $7,12\text{-CB}_{11}\text{H}_{10}\text{Br}_2$ ,  $7,12\text{-CB}_{11}\text{H}_{10}\text{I}_2$ , 7, 8, 9, 10,  $12\text{-CB}_{11}\text{H}_7\text{C}_{15}$ , and 7, 8, 9, 10, 11,  $12\text{-CB}_{11}\text{H}_6\text{C}_{16}$ , as well as pentafluorooxotellurate ( $\text{OTeF}_5$ ) and related anions.

20 Other useful anions include anions of the formula  $\text{M}(\text{OTeF}_5)_n^{m-}$ , wherein M is selected from Ni, Cu, Zn and Pd; n is either 4 or 6; and m is either 1 or 2.

25 Yet further useful anions include  $\text{PW}_{12}\text{O}_{40}^{3-}$  and related anions, and  $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$  together with related anions.

30 Even further useful anions include the fulleride ion  $\text{C}_{60}^-$ , the relatively stable borate anion  $\text{B}(\text{o-C}_6\text{H}_4\text{O}_2)_2^-$  and the diborane anion  $\text{H}(1,8\text{-(BMe}_2)_2\text{C}_{10}\text{H}_6)^-$ .

The non-nickel transition metal derived catalyst of the catalyst system may be a chromium derived catalyst.

The catalyst system of the process of the invention may be a trimerisation catalyst system.

5       The trimerisation catalyst system may include the ionic liquids as solvent or co-solvent and/or activator together with at least one of a chromium source and a pyrrole-containing compound. Typically the chromium source and pyrrole-containing compound are used in combination.

10       In addition to including at least one of the chromium source and the pyrrole-containing compound, the catalyst system may optionally include one or more of a metal alkyl, a halogen source, and an unsaturated hydrocarbon compound.

15       The chromium source of said catalyst system may consist of one or more organic and/or inorganic chromium compounds, with the chromium oxidation state ranging from 0 to 6.

These chromium compounds are suitably expressed by the general formula  $\text{CrX}_n$ , wherein

20       X may be the same or different and represents an organic or inorganic radical, group or compound; and  
n is an integer from 0 to 6.

25       Where at least one of the X's includes an organic radical, the organic radical may have from about 1 to 20 carbon atoms per radical. Typically such radical is selected from the group consisting of alkyl, alkoxy, ester, ketone and/or amido radicals.

30       Where at least one of the X's include an organic compound, then such organic compound may be selected from the group consisting of an amine compound, a phosphine compound, a phosphine oxide compound, a nitrosyl group, and an ether compound.



Where at least one of the X's include an inorganic radical, then such inorganic radical may be selected from the group consisting of halides, nitrates, and sulphates.

5 In specific examples of the trimerisation catalyst system, the chromium source may include one or more of chromium(III)acetylacetonate, chromium (III) acetate, chromium (III) pyrrolide, chromium (III) 2,2,6,6,tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(N,N'-bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro  
10 (N,N,N',N',N"-pentamethyldiethylenetriamine) chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine, chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate), and chromium (II) chloride.

15

The pyrrole-containing compound of the trimerisation catalyst system includes pyrrole and derivatives thereof.

The term "pyrrole" refers to hydrogen pyrrolide, i.e.  $C_4H_5N$ .

20

A "pyrrolide", for purposes of this specification, is defined as a compound containing a 5-membered, nitrogen containing heterocycle.

25 The derivatives of pyrrole in the trimerisation catalyst system may include substituted pyrrolides, heteroleptic or homoleptic metal pyrrolide complexes, salts, and isotopes thereof.

The pyrrole-containing compounds of the trimerisation catalyst system may have from about 4 to about 20 carbon atoms per molecule.

30

The pyrrole-containing compounds of the trimerisation catalyst system may include hydrogen pyrrolide (pyrrole), sodium pyrrolide, lithium pyrrolide, potassium pyrrolide, caesium pyrrolide, chromium (III) pyrrolides, aluminium-diethyl-pyrrolide, ethyl-aluminium-dipyrrolide, aluminium-tripyrrolide, 2,5-dimethylpyrrole, 3,4-dimethylpyrrole, 3,4-dichloro pyrrole, indole, imidazole, 2-acyl-pyrrole, pyrrolidine, or the like.

The pyrrole-containing compounds of the trimerisation catalyst system may include derivatives of pyrrole having a hydrocarbon group bonded to the pyrrole ring.

These pyrrole-containing compounds having a hydrocarbon group bonded to the pyrrole ring are believed to enhance the activity and selectivity of the trimerisation catalyst system to desired products.

The pyrrole-containing compound can be either affirmatively added to the reaction, or generated in-situ.

The catalyst system of the process of the invention may optionally include one or more metal alkyls.

The metal alkyl may be any heteroleptic or homoleptic metal alkyl compound.

Typically, the alkyl ligands include any saturated aliphatic radical.

The alkyl ligands on the metal may be aliphatic or aromatic.

The metal alkyl may have any number of carbon atoms, however, typically less than about 20 carbon atoms per molecule.

The metal alkyl may be selected from the group including, alkyl aluminium compounds, hydrolysed alkyl aluminium compounds, aluminoxanes, alkyl boron compounds, alkyl magnesium compounds, alkyl zinc compounds, and alkyl lithium compounds.

Typically, the metal alkyl is an alkyl aluminium compound, hydrolysed alkyl aluminium compound, or an alkyl boron compound.

Usually the metal alkyl is an alkyl aluminium compound, selected from alkyl aluminium compounds expressed by the formula:  $AlX_nR_{3-n}$  or  $R_nAlOR_{3-n}$ , wherein  
n is an integer selected from 0, 1, 2 and 3;  
R is an alkyl group; and  
X is a halogen atom.

In specific embodiments, the alkyl aluminium compounds include trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride, diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, or the like, and mixtures thereof.

The use of said alkyl aluminium compound is believed to aid catalyst system activity and/or reduce the quantity of undesirably by-product polymer.

Furthermore, the catalyst system may optionally include one or more halogen sources. The optional halogen sources are believed to increase selectivity towards the formation of desired products.

The one or more halogen sources may be selected from any compound containing one or more halogen atoms.

The one or more halogen sources include compounds with the general formula of  $L_mR_nX_p$ , wherein

5 L denotes a cation containing an element selected from those elements belonging to the 1-, 6-, 8-, 9-, 10-, 11-, 13-, 15- and 17-Groups of the Periodic Table;

R may be any organic and/or inorganic radical;

X may be a halide, selected from the group consisting of fluoride, chloride, bromide, and iodide;

m is an integer ranging from 0 to 2;

10 p may be any integer greater than 0; and

n may be any integer, typically less than 100.

Where the R of the one or more halogen sources is an organic radical, typically the R is a cyclic or acyclic radical with about 1 to about 70 carbon atoms, usually having from about 1 to 20 carbon atoms per radical.

Where the R of the one or more halogen sources is an inorganic radical, typically the R is selected from those elements belonging to the 3-, 4-, 5-, 6-, 13-, 14- and 15-Groups of the Periodic Table.

20

The one or more halogen source may include one or more of the other components of the catalyst system including the chromium source, the metal alkyl and the electron pair donor solvent can contain and provide a halide to the reaction mixture.

25

In specific embodiments of the catalyst system the one or more halogen sources may be selected from the group including methylene chloride, chloroform, 1-bromobutane, 1,4-dibromobutane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 5 hexachloroethane, hexachloro-benzene, 1,2,3-trichloro-cyclopropane, 1,2,3-trichlorocyclopentane, zirconium tetrachloride, titanium tetrachloride, silane tetrachloride, tin tetrachloride, aluminium trichloride, boron trichloride, germanium tetrachloride, diethyl aluminium chloride, diethyl aluminium bromide, ethyl aluminium dichloride, 1-chloro-2-butene, allylchloride, tris (pentafluorophenyl)boron, potassium 10 tetrakis (pentafluorophenyl)borate, potassium tetrafluoroaluminate, potassium tetrachloroaluminate potassium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, potassium tetrachloroborate, or the like.

The catalyst system may also include a hydrocarbon and/or hydrocarbon 15 derived compound. It is believed that this compound may increase catalyst system activity and/or lower the viscosity of the ionic liquid phase.

The hydrocarbon and/or hydrocarbon derived compound may be any aromatic or aliphatic hydrocarbon compound. 20

The hydrocarbon and/or hydrocarbon derived compound may have any number of carbon compounds per molecule, but usually has less than 20 carbon atoms. The limitation to less than 20 carbon atoms is due to commercial availability and end use.

25 The hydrocarbon and/or hydrocarbon derived compound includes ethylene, 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, xylene, fluorobenzene, cyclohexane, and the like.

It has been found that 1-hexene can be selectively produced by trimerisation of ethylene using a catalyst system comprising a combination of at least a chromium source and a pyrrole-containing compound in the presence of ionic liquids as solvent or co-solvent. In addition, the use of these ionic liquids as solvent for said chromium catalyst system, also selectively produces the trimeric products of longer chain olefins in high yields.

The process of the invention may be used for the trimerisation of ethylene to 1-hexene.

The process of the invention may be used for the trimerisation of longer chain olefins to their respective trimeric products.

The longer chain olefins may have from 2 - 20 carbon atoms.

The trimerisation of olefins having from 2 to 20 carbons, typically from 5 to 15 carbons, may produce a lubricant.

Where the olefins which are trimerised include 1-decene, then the lubricant may have a viscosity index of typically 130 or higher which corresponds to a high quality synthetic base oil like polyalphaolefin.

The longer chain olefins may include Fischer-Tropsch-derived olefins.

Typical process parameters include one or more of:

- one or more chromium sources present in an amount of between 0.1 mmole per litre solvent and 10 mmole per litre solvent;
- one or more pyrrole-containing compounds present in an amount of from 1 to 10 equivalents with respect to the chromium compounds;
- one or more metal alkyls present in an amount of from 3 to 50 equivalents with respect to the chromium compounds;

- one or more halogen sources present in an amount from 1 to 20 equivalents with respect to the chromium compounds;
- a reaction temperature of between 10°C and 130°C; and
- 5 - a reaction pressure of up to 100 Bar.

The process may be carried out in a batch reactor, in a continuous reactor, in a semi-batch reactor, or any other suitable reactor. For example, the process may be carried out in a fluid bed reactor, a slurry bed reactor, a fixed bed reactor, or the  
10 like.

It is believed that ionic liquids form biphasic systems with oligomerisation reagents and products, thereby permitting ease of continuous operation and separation and recycling of the catalyst system comparable to heterogeneous  
15 systems.

### Examples of Performing the Invention

#### Example 1: Ethylene trimerisation in an ionic liquid 20

All procedures were carried out under inert conditions, using pre-dried reagents.

The catalyst system was prepared as follows: 0.06 mmol of chromium(III) ethylhexanoate was combined with 0.18 mmol of 2,5-dimethylpyrrole and 0.9 mmol of triethylaluminium in cyclohexane. The catalyst complex was activated at room  
25 temperature for a period of two hours. A suitable ionic liquid [10 ml] (e.g. [Bmim][Et<sub>3</sub>Al-Cl]) was added to the activated complex, and the mixture was stirred for 15 minutes.

30

This solution, together with 40 ml cyclohexane, was charged to a pressure reactor, fitted with a mechanical stirrer. The reactor temperature was maintained at 100 - 120°C, while the ethylene pressure was kept at 50 bar. Thorough mixing was  
5 ensured by mixing speeds of 700 RPM's and higher.

Upon exit from the reactor, the product/solvent phase was decanted from the ionic liquid / catalyst phase, and the product/solvent phase was analysed by GC. The ionic liquid / catalyst phase could now be recycled.  
10

A catalyst activity of 13500 g product / g Cr / hour was observed. The selectivity towards C<sub>6</sub> products was 64 mass%, while the selectivity observed towards 1-hexene formation was 83 mass%.

15      **Example 2: 1-Decene trimerisation in an ionic liquid**

All procedures were carried out under inert conditions, using Schlenk apparatus and pre-dried reagents.

20      The catalyst system was prepared as follows: 0.06 moles of chromium(III) ethylhexanoate was combined with 0.18 moles of 2,5-dimethylpyrrole and 0.9 moles of triethylaluminium in cyclohexane. The catalyst complex was activated at room temperature for a period of two hours. 2 ml of a suitable ionic liquid such as [Bmim][Et<sub>3</sub>Al-Cl] was added to the activated complex, and the mixture was stirred for  
25 15 minutes.

1-Decene (20 ml) was added to the activated catalyst system, and the mixture was stirred overnight by magnetic stirrer bar. The product/solvent phase was decanted from the ionic liquid / catalyst phase, and the product/solvent phase was  
30 analysed by high temperature GC. The GC indicated C<sub>30</sub> oligomers to be the main products, while the oligomer fraction contained three main isomers. The ionic liquid / catalyst phase could now potentially be recycled.



The product distribution obtained was as follows:

C<sub>10</sub> - 65%

C<sub>20</sub> - 3%

C<sub>30</sub> - 32%

The C<sub>30</sub> trimer fraction was isolated by short path distillation, and the viscosities at -40°C, 40°C and 100°C determined:

Viscosity @ -40°C: 1181.67 cSt

40°C: 12.31 cSt

100°C: 3.21 cSt

The viscosity index (VI) was calculated as 130, indicating that a polyalphaolefin quality lubricant was produced. NMR analyses of the product indicated mainly short chain branching explaining the good low temperature viscometrics.

### Example 3: 1-Pentene trimerisation in an ionic liquid

All procedures were carried out under inert conditions, using Schlenk apparatus and pre-dried reagents.

The catalyst system was prepared as follows: 0.06 mmol of chromium(III) ethylhexanoate was combined with 0.18 moles of 2,5-dimethylpyrrole and 0.9 moles of triethylaluminium in cyclohexane. The catalyst complex was activated at room temperature for a period of two hours. 2 ml of a suitable ionic liquid (e.g. [Bmim][Et<sub>3</sub>Al-Cl]) was added to the activated complex, and the mixture was stirred for 15 minutes.

1-Pentene (12 ml) was added to the activated catalyst system, and the mixture was stirred overnight by magnetic stirrer bar. The product/solvent phase was decanted from the ionic liquid / catalyst phase, and the product/solvent phase was  
5 analysed by high temperature GC. The GC indicated C<sub>15</sub> oligomers to be the main product, while the oligomer fraction contained three main isomers. The ionic liquid / catalyst phase could now potentially be recycled.

The product distribution obtained was as follows:

10

C<sub>5</sub> - 60%C<sub>10</sub> - 3%C<sub>15</sub> - 37%

15

NMR analysis to determine the isomer structures of the product indicated mainly short chain branching.

**Claims:**

1. A hydrocarbon conversion process for converting olefins to longer chain hydrocarbons, the process using a catalyst system including a non-nickel transition metal derived catalyst and one or more ionic liquids at a reaction temperature of between 10°C and 130°C and a reaction pressure of up to 100 Bar.
2. An oligomerisation process for oligomerising olefins to longer chain hydrocarbons, the process using a catalyst system including a non-nickel transition metal derived catalyst and one or more ionic liquids at a reaction temperature of between 10°C and 130°C and a reaction pressure of up to 100 Bar.
3. An oligomerisation process as claimed in claim 2, wherein the ionic liquids are liquid at a temperature below 50°C.
4. An oligomerisation process as claimed in claim 3, wherein the ionic liquids are liquid at a temperature between 15°C and 25°C.
5. An oligomerisation process as claimed in any one of the preceding claims wherein the ionic liquids are non-aqueous ionic liquids.
6. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are used as a solvent / co-solvent for the catalyst.
7. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are used as an activator for the catalyst.
8. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are good solvents for a wide range of both inorganic and organic materials.

9. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are composed of poorly coordinating ions, thereby being highly polar yet non-coordinating solvents.

5

10. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are immiscible with a number of organic solvents and providing a non-aqueous, polar alternative for two-phase systems.

10

11. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids are substantially non-volatile, hence being useable in high-vacuum systems.

15

12. An oligomerisation process as claimed in any one of the preceding claims wherein the ionic liquids include as cation an organic halide salt, an imidazoline, an alkyl-substituted imidazoline salt, a pyridinium, an alkyl-substituted pyridinium salt, a sulfonium, an alkylsulfonium salt, a phosphonium, or an alkyl-substituted phosphonium salt.

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13. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids include as anion compounds of the formula  $R_nMX_{3-n}$  wherein:

R is a  $C_1 - C_6$  alkyl or iso-alkyl radical;

M is aluminium, gallium, boron or iron (III);

25

X is a halogen atom; and

n is 0, 1, 2 or 3.

14. An oligomerisation process as claimed in any one of the preceding claims, wherein the ionic liquids include as anion compounds of the formula  $R_mM_2X_{6-m}$  wherein
- 5        R is a  $C_1 - C_6$  alkyl or iso-alkyl radical;  
         M is aluminium, gallium, boron or iron (III);  
         X is a halogen atom; and  
         m is 1, 2 or 3.
- 10       15. An oligomerisation process as claimed in any one of claims 2 to claim 14, wherein the metal component of the anion compounds, M, is aluminium and n and/or m is three.
16. An oligomerisation process as claimed in claim 15, wherein the anion
- 15       is an alkylaluminium compound.
17. An oligomerisation process as claimed in claim 16, wherein the alkylaluminium is triethylaluminium.
- 20       18. An oligomerisation process as claimed in any one of claims 2 to claim 14, wherein the anion is an alkylaluminoxane.
19. An oligomerisation process as claimed any one of claims 2 to claim 14, wherein the anion is dimethylaluminoxane.
- 25       20. An oligomerisation process as claimed any one of claims 2 to claim 14, wherein the anion is a borate anion such as  $B(C_6F_5)_4^-$ .
- 30       21. An oligomerisation process as claimed in any one of claims 2 to 20, wherein changes in the solvation characteristics of the ionic liquids are achieved by varying the ratio of the cation to anion of the ionic liquids.

22. An oligomerisation process as claimed in any one of claims 13 to 21, wherein the miscibility of the ionic liquids with organic reactants is altered by varying the alkyl chain length of the cation.

23. An oligomerisation process as claimed in any one of claims 2 to 22, wherein the ionic liquids include as anion one or more compound selected from the group including tin and germanium halides,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{FSO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{CF}_3\text{CO}_2^-$ , copper chlorides, ammonium chlorides and phosphonium chlorides.

24. An oligomerisation process as claimed in claim 2, wherein the ionic liquids include as anion large, weakly coordinating anions.

25. An oligomerisation process as claimed in claim 24, wherein the anion is tetraphenylborate ( $\text{BPh}_4^-$ ) and derivatives thereof.

26. An oligomerisation process as claimed in any one of claims 2 to 25, wherein the anions of the ionic liquids are selected from  $\text{B}(\text{p-C}_6\text{H}_4\text{F})_4^-$ ,  $\text{B}(\text{C}_6\text{F}_5)_4^-$ ,  $\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4^-$ ,  $\text{PH}_3\text{BCNBPh}_3^-$ , 1-carba-closo-dodecacarborate ( $\text{CB}_{11}\text{H}_{12}^-$ ) and related anions, 12- $\text{CB}_{11}\text{H}_{11}\text{Cl}^-$ , 12- $\text{CB}_{11}\text{H}_{11}\text{Br}^-$ , 12- $\text{CB}_{11}\text{H}_{11}\text{I}^-$ , 12- $\text{CB}_{11}\text{H}_{11}(\text{C}_6\text{F}_5)^-$ , 7,12- $\text{CB}_{11}\text{H}_{10}$ , 7,12- $\text{CB}_{11}\text{H}_{10}\text{Br}_2$ , 7,12- $\text{CB}_{11}\text{H}_{10}\text{I}_2$ , 7, 8, 9, 10, 12- $\text{CB}_{11}\text{H}_7\text{C}_{15}$ , 7, 8, 9, 10, 11, 12- $\text{CB}_{11}\text{H}_6\text{C}_{16}$ ), and pentafluorooxotellurate ( $\text{OTeF}_5$ ) and related anions.

27. An oligomerisation process as claimed in any one of claims 2 to 26, wherein the anions include anions of the formula  $\text{M}(\text{OTeF}_5)_n^{m-}$ , wherein

M is selected from Ni, Cu, Zn and Pd;

n is either 4 or 6; and

m is either 1 or 2.

28. An oligomerisation process as claimed in any one of claims 2 to 27, wherein the anions are selected from  $\text{PW}_{12}\text{O}_{40}^{3-}$  and related anions, and  $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$  together with related anions.

29. An oligomerisation process as claimed in any one of claims 2 to 28, wherein the anions are selected from the fulleride ion  $C_{60}^-$ , the relatively stable borate anion  $B(o-C_6H_4O_2)_2^-$  and the diborane anion  $H(1,8-(BMe_2)_2C_{10}H_6)^-$ .

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30. An oligomerisation process as claimed in any one of claims 2 to 29, wherein the non-nickel transition metal derived catalyst is a chromium derived catalyst including one or more chromium sources present in an amount of between 0.1 mmole per litre solvent and 10 mmole per litre solvent.

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31. An oligomerisation process as claimed in any one of claims 2 to 30 applied to trimerisation of olefins having from 2 to 20 carbons.

32. A trimerisation process for the trimerisation of olefins having from 2 to 20 carbons, the process including the use of a trimerisation catalyst system which includes ionic liquids as solvent or co-solvent and/or activator together with at least one of a chromium source and a pyrrole-containing compound, wherein the chromium source, if present, is present in an amount of between 0.1 mmole per litre solvent and 10 mmole per litre solvent and/or the pyrrole-containing compound, if present, is present in an amount of from 1 to 10 equivalents with respect to the chromium source, the trimerisation process being carried out at a reaction temperature of between 10°C and 130°C and a reaction pressure of up to 100 Bar.

33. A trimerisation process as claimed in claim 32, wherein the chromium source and pyrrole-containing compound are used in combination.

34. A trimerisation process as claimed in claim 32 or claim 33, wherein in addition to including at least one of the chromium source and the pyrrole-containing compound, the catalyst system includes one or more of a metal alkyl, a halogen source, and an unsaturated hydrocarbon compound, wherein the metal alkyl, if present, is present in an amount of from 3 to 50 equivalents with respect to the chromium compounds and the halogen source, if present, is present in an amount from 1 to 20 equivalents with respect to the chromium compounds.

35. A trimerisation process as claimed in any one of claims 32 to 34, wherein the chromium source consists of one or more organic and/or inorganic chromium compounds, with the chromium oxidation state ranging from 0 to 6.

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36. A trimerisation process as claimed in claim 35, wherein the chromium compounds are expressed by the general formula  $\text{CrX}_n$ , wherein

X may be the same or different and represents an organic or inorganic radical, group or compound; and

10

n is an integer from 0 to 6.

37. A trimerisation process as claimed in claim 36, wherein where at least one of the X's includes an organic radical, the organic radical having from about 1 to 20 carbon atoms per radical.

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38. A trimerisation process as claimed in claim 37, wherein the organic radical is selected from the group consisting of alkyl, alkoxy, ester, ketone and amido radicals.

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39. A trimerisation process as claimed in claim 36, wherein where at least one of the X's includes an organic compound, then such organic compound is selected from the group consisting of an amine compound, a phosphine compound, a phosphine oxide compound, a nitrosyl group, and an ether compound.

25

40. A trimerisation process as claimed in claim 36, wherein where at least one of the X's includes an inorganic radical, then such inorganic radical is selected from the group consisting of halides, nitrates, and sulphates.



41. A trimerisation process as claimed in any one of claims 32 to 40, wherein the chromium source includes one or more of chromium(III)acetylacetonate, chromium (III) acetate, chromium (III) pyrrolide, chromium (III) 2,2,6,6,tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(N,N'-bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro (N,N,N',N',N"-pentamethyldiethylenetriamine) chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate), and chromium (II) chloride.

42. A trimerisation process as claimed in any one of claims 32 to 41, wherein the pyrrole-containing compound includes pyrrole and derivatives thereof including substituted pyrrolides, heteroleptic or homoleptic metal pyrrolide complexes, salts, and isotopes thereof.

43. A trimerisation process as claimed in any one of claims 32 to 42, wherein the pyrrole-containing compound has from about 4 to about 20 carbon atoms per molecule.

44. A trimerisation process as claimed in any one of claims 32 to 43, wherein the pyrrole-containing compounds of the trimerisation catalyst system includes hydrogen pyrrolide (pyrrole), sodium pyrrolide, lithium pyrrolide, potassium pyrrolide, caesium pyrrolide, chromium (III) pyrrolides, aluminium-diethyl-pyrrolide, ethyl-aluminium-dipyrrolide, aluminium-tripyrrolide, 2,5-dimethylpyrrole, 3,4-dimethylpyrrole, 3,4-dichloro pyrrole, indole, imidazole, 2-acyl-pyrrole, pyrrolidine, and pyrrole derivatives having a hydrocarbon group bonded to the pyrrole ring.

45. A trimerisation process as claimed in any one of claims 32 to 44, wherein the pyrrole-containing compound is affirmatively added to the process.

46. A trimerisation process as claimed in any one of claims 32 to 44, wherein the pyrrole-containing compound is generated in-situ.

47. A trimerisation process as claimed in any one of claims 32 to 46,  
5 wherein the catalyst system includes one or more metal alkyls.

48. A trimerisation process as claimed in claim 47, wherein the metal alkyl is selected from heteroleptic or homoleptic metal alkyl compounds.

10 49. A trimerisation process as claimed in claim 47, wherein the metal alkyl is selected from the group including, alkyl aluminium compounds, hydrolysed alkyl aluminium compounds, aluminoxanes, alkyl boron compounds, alkyl magnesium compounds, alkyl zinc compounds, and alkyl lithium compounds.

15 50. A trimerisation process as claimed in claim 47, wherein the metal alkyl is an alkyl aluminium compound, selected from alkyl aluminium compounds expressed by the formula:  $AlX_nR_{3-n}$  or  $R_nAlOR_{3-n}$ , wherein  
n is an integer selected from 0, 1, 2 and 3;  
R is an alkyl group; and  
20 X is a halogen atom.

51. A trimerisation process as claimed in claim 50, wherein the alkyl aluminium compounds include trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride,  
25 diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, and mixtures thereof.

52. A trimerisation process as claimed in any one of claims 32 to 51, wherein the catalyst system includes one or more halogen sources.

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53. A trimerisation process as claimed in claim 52, wherein the one or more halogen sources include compounds with the general formula of  $L_mR_nX_p$ , wherein

5 L denotes a cation containing an element selected from those elements belonging to the 1-, 6-, 8-, 9-, 10-, 11-, 13-, 15- and 17-Groups of the Periodic Table;

R may be any organic and/or inorganic radical;

X may be a halide, selected from the group consisting of fluoride, chloride, bromide, and iodide;

10 m is an integer ranging from 0 to 2;

p may be any integer greater than 0; and

n may be any integer, typically less than 100.

54. A trimerisation process as claimed in claim 53, wherein where the R of  
15 the one or more halogen sources is an organic radical, then R has from about 1 to about 70 carbon atoms.

55. A trimerisation process as claimed in claim 53, wherein where the R of  
20 the one or more halogen sources is an inorganic radical, then the R is selected from those elements belonging to the 3-, 4-, 5-, 6-, 13-, 14- and 15-Groups of the Periodic Table.

56. A trimerisation process as claimed in claim 52, wherein the one or more halogen sources include one or more of the other components of the catalyst  
25 system including the chromium source, the metal alkyl and the electron pair donor solvent which contain and provide the halide to the process.

57. A trimerisation process as claimed in claim 52, wherein the one or more halogen sources are selected from the group including methylene chloride, chloroform, 1-bromobutane, 1,4-dibromobutane, 1,1,1-trichlorethane, 1,1,2,2-tetrachloroethane, hexachloroethane, hexachloro-benzene, 1,2,3-trichloro-cyclopropane, 1,2,3-trichlorocyclopentane, zirconium tetrachloride, titanium tetrachloride, silane tetrachloride, tin tetrachloride, aluminium trichloride, boron trichloride, germanium tetrachloride, diethyl aluminium chloride, diethyl aluminium bromide, ethyl aluminium dichloride, 1-chloro-2-butene, allylchloride, tris (pentafluorophenyl)boron, potassium tetrakis (pentafluorophenyl)borate, potassium tetrafluoroaluminate, potassium tetrachloroaluminate, potassium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, and potassium tetrachloroborate.

58. A trimerisation process as claimed in any one of claims 32 to 57, wherein the catalyst system includes a hydrocarbon and/or hydrocarbon derived compound.

59. A trimerisation process as claimed in claim 58, wherein the hydrocarbon and/or hydrocarbon derived compound includes ethylene, 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, xylene, fluorobenzene, and cyclohexane.

60. 1-hexene produced by the trimerisation of ethylene according to a trimerisation process as claimed in any one of claims 32 to 59.

61. A lubricant produced by the trimerisation of olefins having from 2 to 20 carbons by trimerisation process as claimed in any one of claims 32 to 59.

62. A lubricant as claimed in claim 61, wherein the olefins which are trimerised have from 5 to 15 carbons.

63. A lubricant as claimed in claim 61 or claim 62 wherein the olefins include 1-decene and the lubricant has a viscosity index of at least 130.

64. A lubricant as claimed in any one of claims 61 to 63 wherein the olefins which are trimerised are Fischer-Tropsch olefins.

5 65. A hydrocarbon conversion process for converting olefins to longer chain hydrocarbons, substantially as herein described and illustrated.

66. An oligomerisation process for oligomerising olefins to longer chain hydrocarbons, substantially as herein described and illustrated,

10 67. A trimerisation process for the trimerisation of olefins having from 2 to 20 carbons, substantially as herein described and illustrated.

68. 1-hexene produced by the trimerisation of ethylene, substantially as  
15 herein described and illustrated.

69. A lubricant produced by the trimerisation of olefins, substantially as herein described and illustrated.

# INTERNATIONAL SEARCH REPORT

I. National Application No

PCT/ZA 00/00233

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C2/32 C08F10/00 C10G50/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08F C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 558 187 A (BP CHEM INT LTD) 1 September 1993 (1993-09-01) the whole document	1-59
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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